

# Perchlorate Radiolysis on Mars and the Origin of Martian Soil Reactivity

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## Abstract

Results from the Viking biology experiments indicate the presence of reactive oxidants in martian soils that have previously been attributed to peroxide and superoxide. Instruments on the Mars Phoenix Lander and the Mars Science Laboratory detected perchlorate in martian soil, which is nonreactive under the conditions of the Viking biology experiments. We show that calcium perchlorate exposed to gamma rays decomposes in a CO<sub>2</sub> atmosphere to form hypochlorite (ClO<sup>-</sup>), trapped oxygen (O<sub>2</sub>), and chlorine dioxide (ClO<sub>2</sub>). Our results show that the release of trapped O<sub>2</sub> (g) from radiation-damaged perchlorate salts and the reaction of ClO<sup>-</sup> with amino acids that were added to the martian soils can explain the results of the Viking biology experiments. We conclude that neither hydrogen peroxide nor superoxide is required to explain the results of the Viking biology experiments. **Key Words:** Mars—Radiolysis—Organic degradation—*in situ* measurement—Planetary habitability and biosignatures. *Astrobiology* 13, 515–520.

## 1. Introduction

EXPERIMENTS PERFORMED during the Viking Mars mission indicated the presence of low levels of reactive oxidants in the Viking soils (Klein *et al.*, 1976). In the Viking Gas Exchange (GEx) experiment, the release of 70–700 nmol of O<sub>2</sub> (g) was measured when 1 cm<sup>3</sup> soil samples were exposed to water (Oyama and Berdahl, 1977). In the Viking Labeled Release (LR) experiment, ~30 nmol of <sup>14</sup>C-labeled gas was produced due to the partial decomposition of an aqueous mixture of <sup>14</sup>C-labeled organics that was added to 0.5 cm<sup>3</sup> of soil (Levin and Straat, 1976). Heat treatment indicated that the origin of GEx and LR results is likely different; by using a protocol intended to sterilize the soil, the GEx oxygen release was determined to be thermally stable, while the species responsible for the LR results was decomposed by heat (Klein, 1978). Since the return of the Viking results, explanations have focused on the possible UV-induced formation and presence of hydrogen peroxide as the thermally unstable LR oxidant and superoxide as the thermally stable GEx oxidant (Oyama *et al.*, 1977). It has also been suggested that the diffusion of these species in the regolith is responsible for subsurface oxidation (Bullock *et al.*, 1994; Yen *et al.*, 2000) and explains the apparent lack of organics in samples measured by the Viking Gas

Chromatograph Mass Spectrometer (GCMS) (Biemann *et al.*, 1977). Although numerous variations on these hypotheses have been presented since the Viking mission, none have been demonstrated to be completely consistent with all aspects of these two experiments (Zent and McKay, 1994; ten Kate, 2010).

Three decades after Viking, the Wet Chemistry Laboratory on the NASA Phoenix Mars Lander measured perchlorate anions (ClO<sub>4</sub><sup>-</sup>) at ~0.5 wt % levels, likely present in the soil as Ca(ClO<sub>4</sub>)<sub>2</sub> and/or Mg(ClO<sub>4</sub>)<sub>2</sub> (Hecht *et al.*, 2009). Recently, samples collected from the Rocknest site by the Mars Science Laboratory (MSL) and analyzed by using the Sample Analysis at Mars (SAM) instrument suite have been found to contain perchlorate (Archer *et al.*, 2013). Although perchlorate salts can behave as strong oxidants at elevated temperatures, their stability under the conditions of the GEx and LR preclude them from directly explaining the results of these experiments. However, we demonstrate that products formed during the decomposition of perchlorate by ionizing radiation can explain the results of the LR and GEx experiments. Due to the thin atmosphere and lack of a planetary magnetosphere on Mars, galactic cosmic rays and solar energetic particles are only slightly attenuated before reaching the surface. The adsorbed radiation dose in the martian

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regolith at the Viking sampling depth of 10–20 cm has been estimated to be  $\sim 0.1$  Gy/year, and galactic cosmic ray penetration extends down to  $\sim 2$  m in the regolith (Dartnell *et al.*, 2007).

We have characterized radiolysis products of  $\text{Ca}(\text{ClO}_4)_2$  that were partially decomposed, in  $\text{CO}_2$  (g) at Mars-like pressures with a  $^{60}\text{Co}$  gamma-ray source. We show that ionizing radiation decomposes perchlorate into lower-oxidation-state oxychlorine and oxygen species, including hypochlorite ( $\text{ClO}^-$ ), chlorine dioxide ( $\text{ClO}_2$ ), and oxygen gas ( $\text{O}_2$ ), that can explain the Viking GEx and LR results. We demonstrate that the primary release of  $^{14}\text{C}$  observed in the LR experiment can be reproduced by the decomposition of chloroalanine formed by the reaction of soil hypochlorite with the  $^{14}\text{C}$ -labeled alanine present in the LR organic medium. We also show that release of  $\text{O}_2$  (g) trapped in radiation-damaged perchlorate salt can explain the GEx results.

## 2. Methods

Anhydrous calcium perchlorate was prepared from calcium perchlorate tetrahydrate (Sigma Aldrich, 99%; CAS 15627-86-8) by dehydrating 0.5 g samples, in 5 mL glass ampules (Wheaton, 651509), under vacuum at  $200^\circ\text{C}$  for 8–10 h. After the dehydrated samples were allowed to cool under vacuum to room temperature, the ampules were backfilled to  $7.5 \pm 0.2$  mbar with  $\text{CO}_2$  gas (Scott, UHP 99.999%) and flame sealed. The sealed samples were exposed to gamma radiation at room temperature with a  $^{60}\text{Co}$  source at a rate of  $50 \text{ kGy h}^{-1}$  for a total dose of 500 kGy. The samples remained at ambient temperature for  $\sim 2$  days during transit from the radiation facility (Sterigenics Inc., CA). Since heat can accelerate product (*e.g.*, hypochlorite) decomposition, upon return the samples were stored in the still sealed ampules at  $-20^\circ\text{C}$  until just prior to analysis.

After irradiation, hypochlorite and chlorine dioxide concentrations were determined by measuring the UV absorbance spectra of the gamma-irradiated samples in aqueous solution. Concentrations were determined as a function of time by using a molar extinction coefficient of  $350 \text{ L mol}^{-1} \text{ cm}^{-1}$  at 290 nm for hypochlorite and  $1250 \text{ L mol}^{-1} \text{ cm}^{-1}$  at 360 nm for chlorine dioxide. Absorbance measurements were made with an Ocean Optics HR2000 UV-vis-NIR spectrometer, an Ocean Optics HD2000 UV-vis-NIR light source, a 1 cm cuvette, and associated optical fibers. Since the pH of Phoenix and Viking soils is slightly basic (Quinn and Orenberg, 1993; Kounaves *et al.*, 2010), the irradiated perchlorate products were measured in a slightly basic aqueous solution (pH 9 borax buffer).

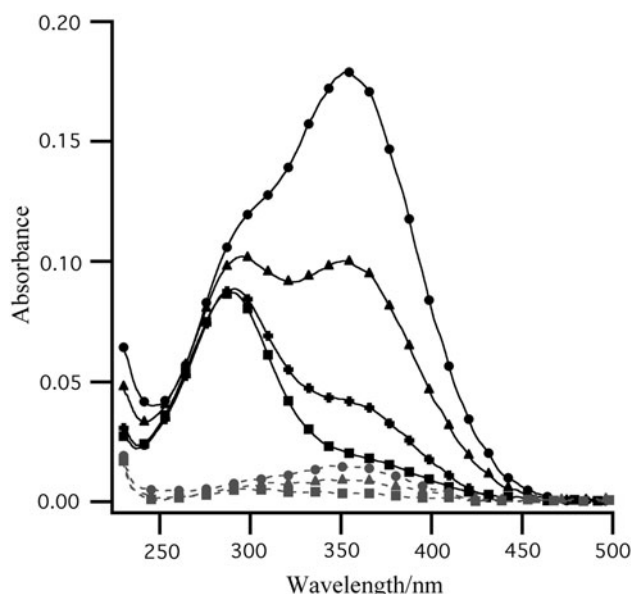
Hypochlorite and chlorine dioxide concentrations were also independently quantified by measurement of the UV absorbance of tri-iodide formed from the quantitative oxidation of iodide to tri-iodide in aqueous solution (Prince, 1964). Hypochlorite and chlorine dioxide were first measured by adding irradiated perchlorate to KI (1%) in sodium borate (pH 9), followed by measurement of the 350 nm tri-iodide absorption. At pH 9, hypochlorite is completely reduced to chloride, and chlorine dioxide undergoes a one-electron reduction to chlorite. After measuring the 350 nm absorbance at pH 9, the solution was acidified to a pH of 1.5. Under acidic conditions, chlorite (in this case formed from chlorine dioxide reduction at pH 9) reacts with iodide and is

reduced to chloride. Hypochlorite and chlorine dioxide concentrations were then calculated from the difference in the pH 9 and pH 1.5 tri-iodide absorbances.

To measure the production of  $\text{O}_2$  (g) and  $\text{CO}_2$  (g) by the irradiated perchlorate samples upon addition of aqueous organics,  $\sim 100$  mg samples were transferred under dry-He into 10 cc glass vials and crimp sealed with rubber septa. The quantity of  $\text{O}_2$  (g) and  $^{13}\text{CO}_2$  (g) produced after the addition of  $^{13}\text{C}$ -labeled alanine ( $2.5 \times 10^{-3} \text{ M}$ ) was determined by periodically sampling the vial headspace with a gas-tight syringe, followed by gas chromatography–mass spectroscopic analysis of the extracted gases.  $^{13}\text{C}$ -labeled alanine was used to differentiate  $\text{CO}_2$  production due to alanine decomposition from background  $\text{CO}_2$  (primarily  $^{12}\text{CO}_2$ ).

Ultraviolet spectroscopy was used to confirm that observed rate of labeled- $\text{CO}_2$  production corresponded to *N*-chloroamino acid decomposition. The 255 nm absorbance due to *N*-chloroamino acids formed after the addition of reagent  $\text{Ca}(\text{ClO})_2$  to a  $5.0 \times 10^{-4} \text{ M}$  alanine and  $2.5 \times 10^{-4} \text{ M}$  glycine solution was measured to determine the decomposition rates. During experimental runs, sample temperature was held at  $10^\circ\text{C}$  to approximate the temperature of the Viking biology experiments. The thermal stability of the perchlorate decomposition products was evaluated by heating sealed samples at  $160^\circ\text{C}$  for 3 h to mimic the LR heat treatment protocol. After cooling to  $10^\circ\text{C}$ , the heat-treated samples were analyzed in the same manner as the other samples.  $\text{Ca}(\text{ClO}_4)_2$  samples, prepared as described above, that were not exposed to gamma irradiation served as control samples.

The Viking LR data was obtained from the NASA Planetary Data System. The data sets contain the counts recorded by a



**FIG. 1.** UV spectra of gamma-irradiated  $\text{Ca}(\text{ClO}_4)_2$  in an aqueous pH 9 buffered solution ( $20^\circ\text{C}$ ).  $\epsilon_{\text{max}} = 360 \text{ nm}$  for  $\text{ClO}_2$  (g), and  $\epsilon_{\text{max}} = 290 \text{ nm}$  for  $\text{ClO}^-$  (aq). A decrease absorbance at 360 nm occurs due to the loss of  $\text{ClO}_2$  (g) from solution. Only residual levels of  $\text{ClO}_2$  (g) remain in samples heated to  $160^\circ\text{C}$  (unheated:  $\bullet$  0 min;  $\blacktriangle$  40 min;  $\blacksquare$  80 min;  $\blacksquare$  120 min; heated:  $\bullet$  0 min;  $\blacktriangle$  40 min;  $\blacksquare$  120 min).

TABLE 1. CALCIUM PERCHLORATE RADIOLYSIS PRODUCTS AND YIELDS<sup>a</sup>

Product	$\text{Ca}(\text{ClO}_4)_2$				$(\text{CaClO}_4)_2$ heated			
	mol %	$\sigma^b$	$G^c$	$\sigma$	mol %	$\sigma$	$G^c$	$\sigma$
$\text{ClO}_2^-$	0.00	0.00	0.00	0.00	0.00	0.00	N.A.	N.A.
$\text{ClO}^-$	0.020	0.003	0.032	0.005	0.00	0.00	N.A.	N.A.
$\text{ClO}_2$	0.068	0.005	0.109	0.007	0.02	0.002	N.A.	N.A.
$\text{O}_2$	1.0	0.1	1.6	0.2	0.83	0.02	N.A.	N.A.
$^{13}\text{CO}_2^d$	0.022	0.003	N.A.	N.A.	0.00	0.00	N.A.	N.A.

<sup>a</sup>Reported as mol % relative to initial  $\text{ClO}_4^-$ .

<sup>b</sup>Standard deviation.

<sup>c</sup>Number of molecules produced per 100 eV of absorbed energy.

<sup>d</sup>Based on the  $^{13}\text{CO}_2$  released after addition of  $^{13}\text{C}$  labeled LR organics to irradiated  $\text{Ca}(\text{ClO}_4)_2$ .

N.A., not applicable.

solid-state beta detector as a function of time resulting from the presence of  $^{14}\text{C}$ -labeled gas in the sample cell headspace.

### 3. Results

Figure 1 shows UV spectra of  $\text{Ca}(\text{ClO}_4)_2$  added to pH 9 solution after a  $\sim 500$  kGy irradiation dose. Both  $\text{ClO}^-$  and  $\text{ClO}_2$  are identified by their absorbances at 290 and 360 nm, respectively. We attribute the 360 nm absorbance decrease over the duration of the measurements to the loss of  $\text{ClO}_2$  (g) from solution, rather than decomposition. In basic conditions, the reduction of  $\text{ClO}_2$  (g) results in the formation of chlorite ( $\text{ClO}_2^-$ ), which has an absorbance at 260 nm. The absence of a 260 nm absorbance indicates that chlorite is not formed in solution and that  $\text{ClO}_2^-$  is not an end product of the  $\text{Ca}(\text{ClO}_4)_2$  radiolysis.

Table 1 reports the levels of  $\text{ClO}^-$  and  $\text{ClO}_2$  measured in irradiated  $\text{Ca}(\text{ClO}_4)_2$  and in irradiated  $\text{Ca}(\text{ClO}_4)_2$  that was heated for 3 h at  $160^\circ\text{C}$  prior to analysis. No  $\text{ClO}^-$  and only trace levels of  $\text{ClO}_2$  were measured in samples that were heat treated. Also shown in Table 1 is the quantity of  $\text{O}_2$  (g) and  $^{13}\text{CO}_2$  (g) released from irradiated perchlorate samples upon wetting with  $^{13}\text{C}$ -labeled LR organics. The quantity of  $^{13}\text{CO}_2$  produced is equal to the amount of  $\text{ClO}^-$  present in the irradiated sample, suggesting that  $\text{ClO}_2$  does not contribute to organic decomposition. The amount of  $\text{O}_2$  released from samples that were heat treated prior to analysis was only slightly lower than the amount from samples that were not heated, a result that is consistent with the Viking GEx experiment.

The Viking LR nutrient medium contained seven isotopically labeled organic compounds (sodium formate, D-alanine, L-alanine, sodium D-lactate, sodium L-lactate, glycine, and calcium glycolate), each at a concentration of  $2.5 \times 10^{-4}$  M (Klein *et al.*, 1976). Upon addition of irradiated  $\text{Ca}(\text{ClO}_4)_2$  to the aqueous LR organics, an absorption at 255 nm rapidly appears due to the formation of *N*-chloroamino acids (Fig. 2). Under the Viking LR experiment conditions, based on the second-order rate constants for the chlorination of alanine and glycine,  $\sim 30$  nmol of  $\text{ClO}^-$  will react to 99% completion with the alanine and glycine in the LR nutrient in less than 210 ms (Pattison *et al.*, 2003). The rapid scavenging of  $\text{ClO}^-$  by the amino acids prevents its reaction with formate, lactate, or glycolate. When aqueous alanine solution is added to gamma-irradiated  $\text{Ca}(\text{ClO}_4)_2$ , the observed increase in headspace  $\text{CO}_2$  closely matches the Viking

LR results (Fig. 3). As was the case in the Viking LR experiments, no  $\text{CO}_2$  release was observed from samples heated to  $160^\circ\text{C}$ . However, the heat-treated samples did release  $\text{O}_2$  (g), as was observed in the Viking GEx experiment (Table 1).

Following rapid formation, *N*-chloroalanine and *N*-chloroglycine decompose through pH-independent (from pH 5 to 9) first-order reaction mechanisms with the rate of *N*-chloroglycine decomposition being  $\sim 2\%$  relative to the rate of *N*-chloroalanine decomposition (Hand *et al.*, 1983). Our tests in which reagent  $\text{Ca}(\text{ClO})_2$  was added to solutions containing both alanine and glycine at  $\sim 10^\circ\text{C}$  indicated that *N*-chloroalanine is the primary chlorination product (Fig. 3). However, it may be possible that in the LR experiment on

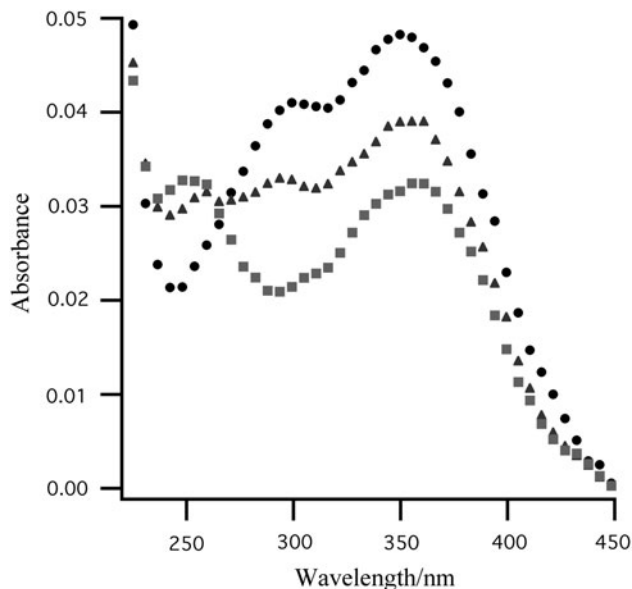


FIG. 2. The rapid formation of *N*-chloroamino acids (255 nm) upon addition of Viking LR organics to gamma-irradiated  $\text{Ca}(\text{ClO}_4)_2$  in aqueous solution ( $\bullet$  0 s;  $\blacktriangle$  0.16 s;  $\blacksquare$  0.32 s). The absorbance by  $\text{ClO}^-$  at 290 nm decreases as *N*-chloroamino acids form (260 nm). The absorbance by  $\text{ClO}_2$  (g) at 360 nm is attenuated due to dilution by the addition of the LR organics. No reaction between the LR organics and  $\text{ClO}_2$  (g) is observed. The LR aqueous organic solution contains sodium formate, D-alanine, L-alanine, sodium D-lactate, sodium L-lactate, glycine, and calcium glycolate, each at a concentration of  $2.5 \times 10^{-4}$  M.

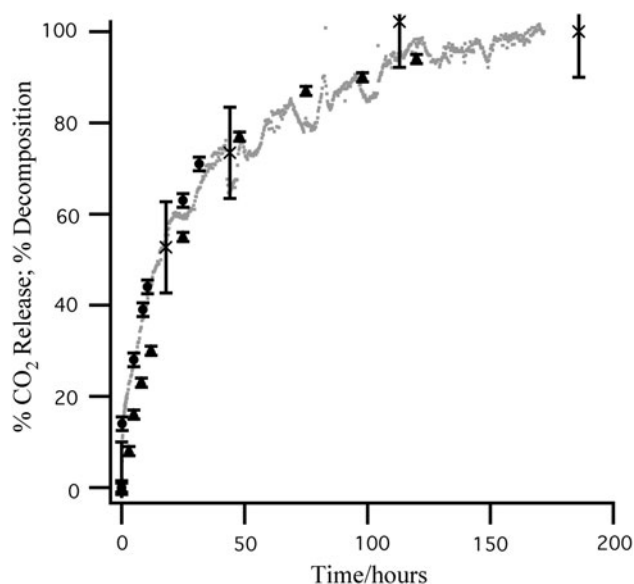


FIG. 3. Viking LR gas release (VL2C3 ●) compared to  $^{13}\text{CO}_2$  (g) released from aqueous  $^{13}\text{C}$ -alanine after addition to gamma-irradiated  $\text{Ca}(\text{ClO}_4)_2$  (×). No  $^{13}\text{CO}_2$  release was observed from samples heated to  $160^\circ\text{C}$ . Also shown is the decomposition of chloroamino acids [initial concentrations  $4.0 \times 10^{-4} \text{ M}$  (▲) and  $2.0 \times 10^{-4} \text{ M}$  (●)] formed after the addition of  $\text{Ca}(\text{ClO})_2$  to a  $5.0 \times 10^{-4} \text{ M}$  alanine and  $2.5 \times 10^{-4} \text{ M}$  glycine solution. The chloroamino acid decomposition rate compared to the  $^{13}\text{CO}_2$  release rate suggests that chloroalanine is the primary chlorination product.

Mars *N*-chloroglycine formation was higher. If this is the case, *N*-chloroglycine decomposition may contribute to the slower secondary labeled gas release that was observed in the Viking LR. This slow secondary gas release in the LR has previously been attributed to the decomposition of organics by iron oxide (Levin and Straat, 1979).

#### 4. Discussion

Prior to the Phoenix mission, the possible presence of perchlorates or other oxyhalides on Mars in the context of the Viking results and the preservation of biomarkers had not been rigorously considered. The possibility that Mars soil may contain perchlorates was recognized, but the instruments on missions prior to Phoenix lacked the capability to distinguish between different forms of chlorine (Clark *et al.*, 2005). It has been suggested that thermodynamically unstable species formed on UV-activated surfaces of halide evaporites could be responsible for  $\text{O}_2$  generation in the GEx experiment; however, the presence of bulk  $\text{O}_2$  (g) in martian soil was discounted (Zent and McKay, 1994).  $\text{O}_2$  (g) trapped in soil pore space and released upon humidification by the Rebiner effect has been previously proposed as an explanation for the GEx experiment (Nussinov *et al.*, 1978). However, perchlorate radiolysis has not previously been proposed as the origin and trapping mechanism of  $\text{O}_2$  (g) in the martian regolith. Our results suggest that the  $\text{O}_2$  (g) is trapped in the radiation-damaged salt and is released upon water-induced dissolution.

Plumb *et al.* (1989) proposed that nitrate partially photolyzed by UV light in the presence of calcite could explain the

GEx and LR results. Although calcite has been identified at the Phoenix site, nitrates have not been identified on Mars. However, if present, nitrate like perchlorate is decomposed by ionizing radiation (*e.g.*, Hennig *et al.*, 1953) and may contribute to the reactive nature of the martian soil.

In addition to chlorine dioxide and hypochlorite formation, radiolysis of alkali and alkaline Earth perchlorates [*e.g.*,  $(\text{MgClO}_4)_2$ ] can also result in the formation of chlorate and chlorite (Prince and Johnson, 1965). The presence of perchlorate radiolysis products in martian soils presents a number of important ramifications for Mars exploration, the habitability of martian soil, and the search for organic compounds. Additionally, processes involving superoxide and peroxide that have been previously proposed based on interpretations of Viking biology results may play a less important role in the oxidative alteration of organics than has previously been suggested. A number of shortcomings of the hypotheses that hydrogen peroxide and superoxide were responsible for the LR and GEx results have been recognized. In particular, due to pH-dependant reaction rates and competitive loss mechanisms, implausibly large amounts of hydrogen peroxide have been required to simulate the LR results (Levin and Straat, 1981).

Hypochlorite and other potentially reactive oxyhalide species can decompose some classes of organic compounds and act as antimicrobial agents (Deborde and von Gunten, 2008); however, on Mars these effects may be limited to areas in close proximity to soils that contain perchlorate. However, given the possible atmospheric origin of perchlorate (Catling *et al.*, 2010), it is likely to be a component of globally distributed dust and may interfere with soil analyses. The presence of perchlorate at the Phoenix (Hecht *et al.*, 2009) and MSL (Archer *et al.*, 2013) landing sites suggests a global distribution. Additionally, although this suggestion is controversial (Biemann and Bada, 2011), reevaluation of the Viking GCMS results after the Phoenix mission suggests that perchlorate interfered with the detection of soil organics (Navarro-González *et al.*, 2010). Likewise, the presence of more reactive lower-oxidation-state oxychlorine species in martian soils may interfere with soil analyses including analyses performed with the SAM instrument on the MSL Curiosity rover (Mahaffy *et al.*, 2012). For example, during thermal analysis, the release of oxygen and reactive chlorine species from the martian soil may occur at temperatures below the decomposition temperature of perchlorate. The detection of chlorohydrocarbons when using the Viking 1 GCMS (Biemann *et al.*, 1977) and MSL SAM instrument suite (Glavin *et al.*, 2013) from martian soils heated to  $200^\circ\text{C}$  supports this possibility. Additionally, our results suggest that fluidic-based derivatization approaches intended to enhance *in situ* amino acid detection may be inhibited by the rapid chlorination of amino acids by  $\text{ClO}^-$  (Skelley *et al.*, 2006; Mahaffy *et al.*, 2012).

#### 5. Conclusions

We conclude that on Mars galactic cosmic rays and solar energetic particles should result in the formation of hypochlorite, other lower-oxidation-state oxychlorine species, and trapped  $\text{O}_2$  (g) in perchlorate-containing soils. Based on our experimental results, we conclude that the decomposition of *N*-chloroalanine formed by the reaction of hypochlorite with



the alanine in Viking LR nutrient medium was the primary source of labeled gas ( $^{14}\text{CO}_2$ ) production in the LR experiment. We also conclude that the  $\text{O}_2$  (g) trapped in radiation-damaged perchlorate salts was the origin of the  $\text{O}_2$  (g) release observed in the Viking GEx experiments. Based on our results, it appears that neither hydrogen peroxide nor superoxide is required to explain Viking LR and GEx experiments.

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### Abbreviations

GCMS, Gas Chromatograph Mass Spectrometer; GEx, Gas Exchange; LR, Labeled Release; MSL, Mars Science Laboratory; SAM, Sample Analysis at Mars.

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